

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

# WARTIME REPORT

ORIGINALLY ISSUED

May 1943 as  
Advance Restricted Report 3E26

LEAD SUSCEPTIBILITY OF PARAFFINS, CYCLOPARAFFINS,  
AND OLEFINS

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## ADVANCE RESTRICTED REPORT

## LEAD SUSCEPTIBILITY OF PARAFFINS, CYCLOPARAFFINS, AND OLEFINS

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## SUMMARY

General relationships for the lead susceptibilities of paraffins, cycloparaffins, and olefins are presented. Methods are described by which the lead response may be estimated for these hydrocarbon classes, whether the lead response is indicated by octane number, critical compression ratio, or indicated mean effective pressure as limited by knock.

## INTRODUCTION

Two disadvantages of the octane scale are the nonlinear nature of the curve and the discontinuity of the scale at 100-octane number. Heron and Beatty (reference 1) have made a significant approach to the correction or elimination of these difficulties by showing that, for supercharged-fuel tests, the relation between the reciprocal of indicated mean effective pressure and octane number is a straight line. Recent data from The Ethyl Corporation uphold this fact, as shown in figure 1. In figure 2 the same data are plotted using the indicated mean effective pressure instead of its reciprocal. The two curves in figures 1 and 2 can be represented by the equation of an equilateral hyperbola

$$P (125 - N) = 3520 \quad (1)$$

where

P maximum permissible indicated mean effective pressure

N supercharged octane number

The relation between critical compression ratio and A.S.T.M. (Motor) Method octane number can also be represented by the equation for a hyperbola. This relation is illustrated in figure 3. The curve in figure 3 was calculated from figure 1 of reference 2 which shows the relationship between height of compression chamber and A.S.T.M. (Motor) Method octane number. The points on the curve

in figure 3 are experimental points from reference 2. The hyperbolic equation for the curve in figure 3 is

$$(R - 3.3) (125 - N_1) = 125 \quad (2)$$

where

R critical compression ratio

$N_1$  A.S.T.M. (Motor) Method octane number

The asymptotes for the curve in figure 3 are 3.3 critical compression ratio and 125 A.S.T.M. (Motor) Method octane number. Since the asymptotes for figure 3 are finite numbers, no straight-line relation can exist between the reciprocal of critical compression ratio and octane number.

It has been shown in unpublished data from this laboratory that, for the relationship of critical compression ratio to octane number, neither of these asymptotes is constant when engine conditions are varied. On a supercharged CFR engine (reference 1) it was found, however, that the relationship between the inverse indicated mean effective pressure and the supercharged octane number remained linear but changed in slope as engine conditions were varied. It follows from this fact that the curve in figure 2 will change in position if engine conditions are varied but that, regardless of engine conditions, the curve will remain asymptotic to zero indicated mean effective pressure.

In figure 4 are plotted data obtained by the A.P.I. Heron and Beatty (reference 1) interpreted lead response (gain of octane number per ml of tetraethyl lead) in terms of straight lines by using a plot similar to figure 4. A relation between figures 3 and 4 may be shown by extending the lines in figure 4 until they intersect at 125-octane number. If both scales of figure 4 were converted to critical compression ratios, the point of intersection of the curves would be at a compression ratio of 3.3, as will be shown later. These points of intersection are the asymptotes of figure 3.

The existence of a straight-line relationship, such as shown in figure 4, has been previously used to show lead response in terms of octane number. It is, however, more desirable to have lead response defined in terms of increase in indicated mean effective pressure or increase in critical compression ratio. These last two methods have been used in the present analysis.

## DISCUSSION OF RESULTS

Supercharged-engine-test data. - By use of the available data, an analysis has been made of the lead response of the paraffins, cycloparaffins, and olefins. The lead response may be represented as a straight line by plotting indicated mean effective pressures of the pure fuels against indicated mean effective pressures of the leaded fuels. This method is used in figures 5 through 14 with the exception of figure 12. The data in figures 5 through 14 were taken at the engine conditions shown in figure 1. In figure 5 the response of the pentanes to 1.0 milliliter of tetraethyl lead is shown. A straight line drawn through these points intersects the 45° line at zero indicated mean effective pressure. The intersection is also at zero for the hexanes, heptanes, octanes, and nonanes shown in figures 6, 7, 8, and 9, respectively.

The lead response of all the paraffins can be represented by a single straight line, as shown in figure 10. It is obvious that the compound having the highest permissible indicated mean effective pressure in the pure state has the greatest lead response. The passage of the line of constant lead concentration in figure 10 through the origin shows that the percentage increase in power for 1.0 milliliter of tetraethyl lead per gallon is constant for all paraffins. Heron and Beatty (reference 1) found this statement to be true for 6.0-milliliter additions of tetraethyl lead.

The susceptibility of isooctane to various quantities of tetraethyl lead is shown in figure 11. It is possible that the lead response of all the paraffins may be represented by a chart similar to figure 11, but the position of the lines for constant tetraethyl-lead concentrations other than 1 milliliter cannot be verified from the available data.

In figure 12 the data from figure 11 are plotted as percentage power based on 100 percent power with isooctane against milliliters of tetraethyl lead. On the same figure are plotted values chosen by the Army Air Forces at Wright Field to define the antiknock requirements of pursuit-grade aviation fuels in terms of performance numbers. The performance numbers are plotted on the same scale used for the power percentages. The values of performance number can be represented by the following equation of a hyperbola:

$$P_n = 187.9 - \frac{232}{2.65 + L} \quad (3)$$

where

$P_n$  performance number

$L$  milliliters of tetraethyl lead per gallon

The curve drawn through the points in figure 12 is calculated from equation (3). The data from figure 11 are in close agreement with this curve.

There are insufficient data to definitely establish the susceptibilities of the cycloparaffins (fig. 13) and olefins (fig. 14). When figures 12, 13, and 14 are compared, the response of the paraffins, cycloparaffins, and olefins is of the following order:

Hydrocarbons (ml TEL/gal)	Percentage increase imep					
	1.0	2.0	3.0	4.0	5.0	6.0
Paraffins	26	36	46	51	57	61
Cycloparaffins	23	----	----	----	----	----
Olefins	14	----	----	----	----	----

The percentage increase in indicated mean effective pressure for the olefins is estimated from diisobutylene.

A.S.T.M. (Motor) Method data. - It has been shown in the introduction of this paper that the curve in figure 3 may be represented by a hyperbola asymptotic to a critical compression ratio of 3.3 and an octane number of 125. It has also been shown that the straight lines in figure 4, if extended, would intersect at an octane number of 125. When the ratings shown in figure 4 are converted to critical compression ratios by figure 3, straight lines are obtained. These lines intersect at a critical compression ratio of 3.3 for the paraffins, cycloparaffins, or olefins.

By the use of critical compression ratios, an analysis similar to that of supercharged-test-engine data has been made for the available hydrocarbon ratings. The lead susceptibilities of the pentanes, hexanes, heptanes, and octanes are shown in figures 15, 16, 17, and 18, respectively. As shown in figures 19 and 20, the lead response of the paraffins may be represented by single straight lines for 1.0 and 3.0 milliliters of tetraethyl lead, respectively. The equation for these straight lines of constant tetraethyl-lead concentration is

$$R_L = K R - 3.3 (K - 1) \quad (4)$$

where

$R_L$  critical compression ratio of leaded fuel

$R$  critical compression ratio of pure fuel

$K$  slope of line of constant tetraethyl-lead concentration

The cycloparaffins (figs. 21 and 22) may also be represented by a single straight line. The lead susceptibility of the olefins shown in figures 23 and 24 is affected by the position of the double bond. Until more data are available, the accuracy of the lines of constant lead concentration cannot be established. When these two figures are compared, it may be said that the octenes having the double bond in the 2 position have greater lead response than those with the double bond in the 1 position.

For each group of hydrocarbons there will be a different value of  $K$  for equation (4). From figures 19, 20, 21, 22, 23, and 24 the following values of  $K$  have been determined:

Hydrocarbon	Value of $K$	
	for 1.0 ml	for 3.0 ml
Paraffins	1.34	1.57
Cycloparaffins	1.24	1.41
Octene - 2	1.22	1.33
Octene - 1	1.13	1.30

Since  $K$  is the slope of the line of constant tetraethyl-lead concentration, it is necessary to determine the lead response of only one compound in a particular hydrocarbon classification in order to estimate the lead response of other compounds of the same type from their pure ratings. The variation of  $K$  with tetraethyl-lead concentration is shown in figure 25.

In figures 19, 20, 21, 22, 23, and 24 the straight lines intersect at a critical compression ratio of 3.3. It seems likely that this point of intersection is fixed for all hydrocarbon types for A.S.T.M. (Motor) Method engine conditions. Unlike supercharged data in which the percentage increase in power is constant for a given quantity of tetraethyl lead regardless of the pure fuel rating, the percentage increase in critical compression ratio for a given quantity of tetraethyl

lead varies with the pure fuel ratings. This variation is illustrated for the paraffins by the curves in figure 26, which are calculated from figures 19 and 20. The fact that the percentage increase of critical compression ratio is not constant adds to the difficulty of interpreting A.S.T.M. (Motor) Method ratings.

### CONCLUSIONS

The following conclusions may be drawn from the results presented in this report:

1. For supercharged-engine tests, the percentage increase in permissible indicated mean effective pressure for a given amount of tetraethyl lead per gallon was constant for the paraffins. This result was also true for the cycloparaffins.

2. For a 1.0-milliliter addition of tetraethyl lead per gallon, the power increase was about 26 percent for paraffins and 23 percent for cycloparaffins at the supercharged-engine conditions examined. An increase of 15 percent was determined for the olefins based on one rating for diisobutylene.

3. At A.S.T.M. (Motor) Method engine conditions, the following equation may be used to estimate lead response:

$$R_L = K R - 3.3 (K - 1)$$

where

$R_L$  critical compression ratio of leaded fuel

$R$  critical compression ratio of pure fuel

$K$  slope of line of constant tetraethyl-lead concentration

For a 1.0-milliliter addition of tetraethyl lead, the value  $K$  obtained for the paraffins is 1.34; for the cycloparaffins, 1.24; for octenes with double bond in the 2 position, 1.22; and for octenes with double bond in the 1 position, 1.13. For a 3.0-milliliter addition, the values of  $K$  obtained for the same compounds is 1.57, 1.41, 1.33, and 1.30, respectively.

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1. Heron, S. D., and Beatty, Harold A.: Aircraft Fuels. Jour. Aero. Sci., vol. 5, no. 12, Oct. 1938, pp. 463-479.
2. Smittenberg, J., Hoog, H., Moerbeek, B. H., and v.d. Zijden, M. J.: Octane Ratings of a Number of Pure Hydrocarbons and Some of Their Binary Mixtures. Jour. Inst. Petroleum, vol. 28, no. 200, June 1940, pp. 294-300.



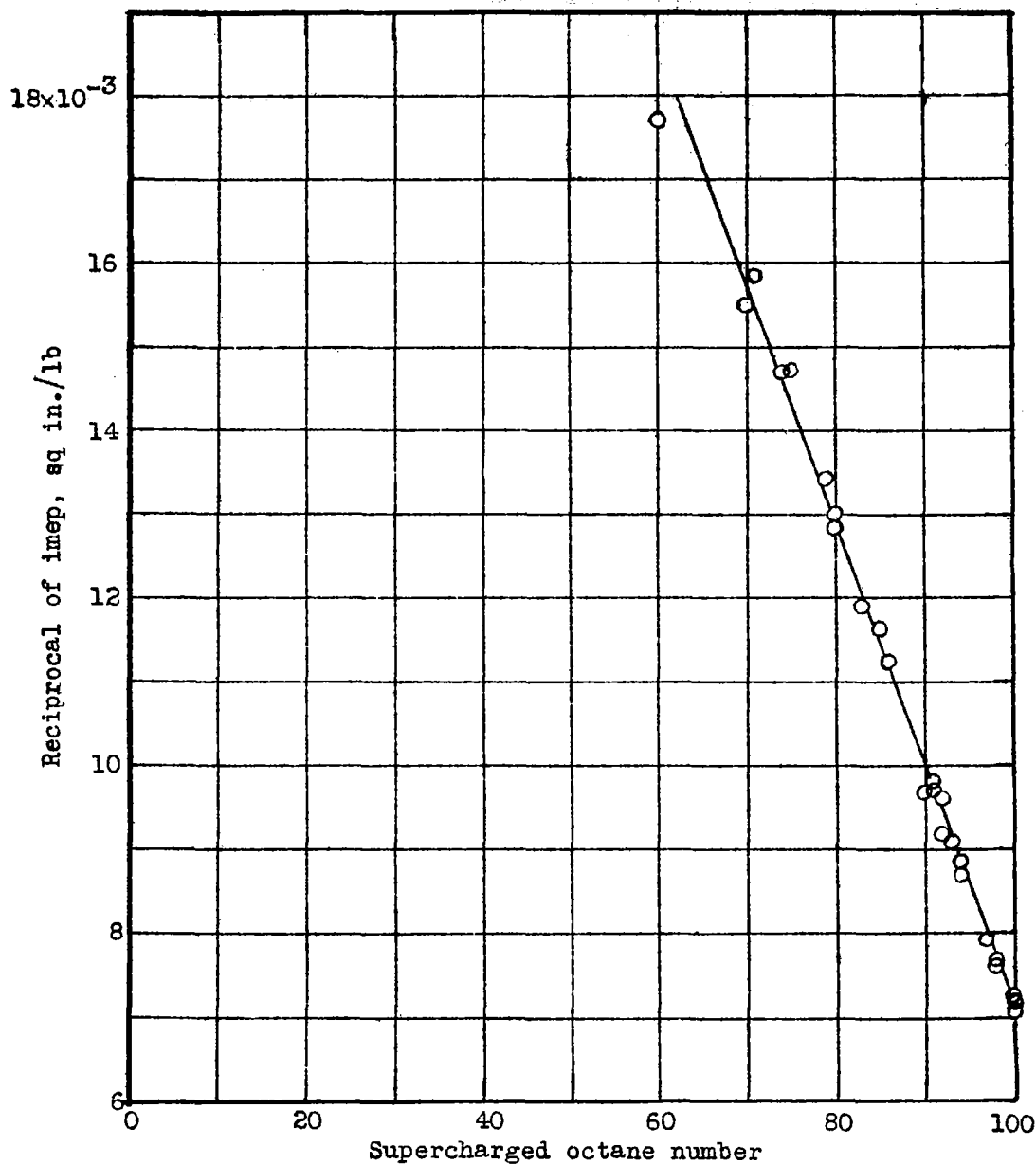


Figure 1.- Variation of reciprocal of indicated mean effective pressure with octane number at supercharged-engine-test conditions. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

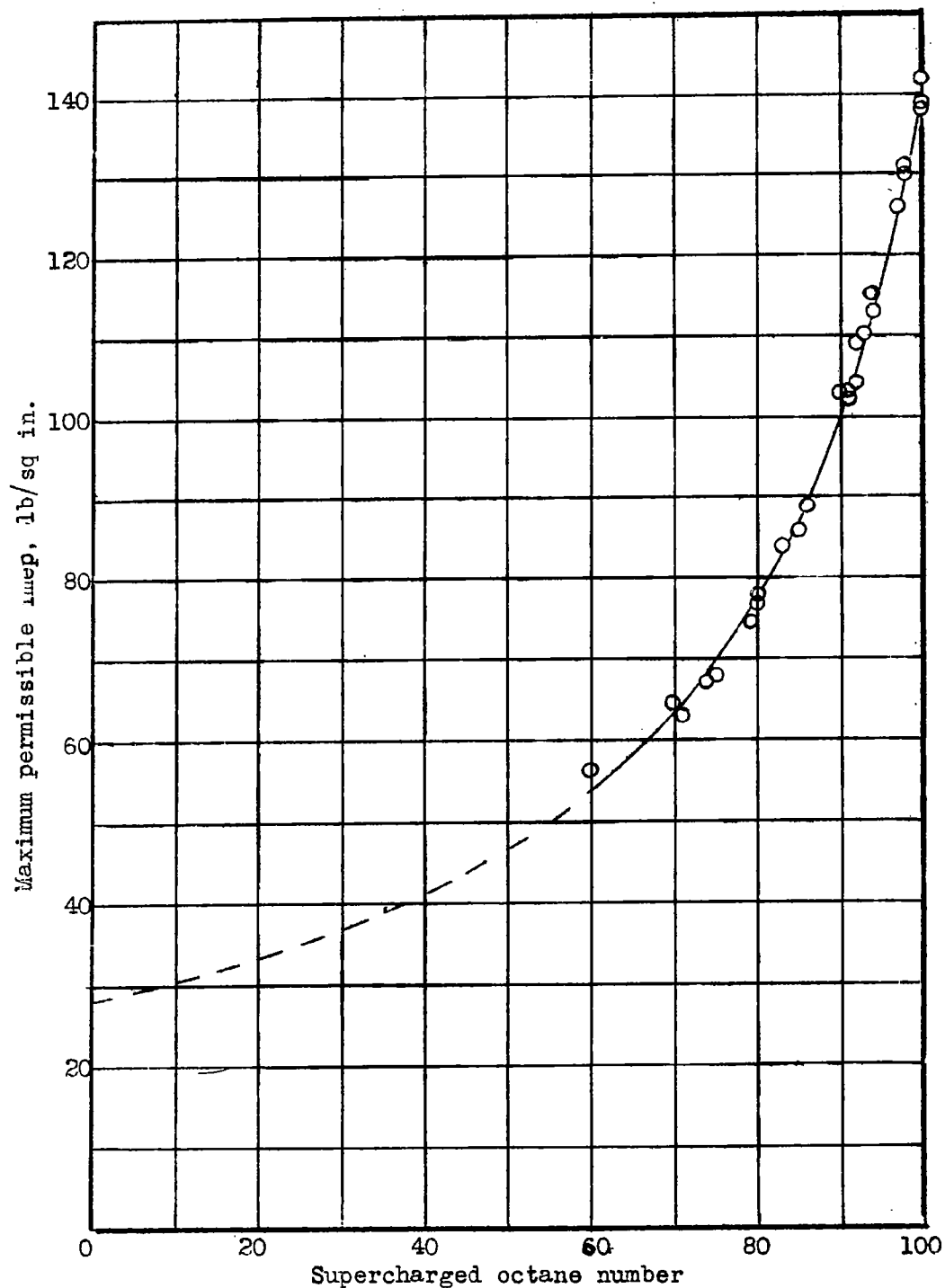


Figure 2.- Variation of indicated mean effective pressure with octane number at supercharged-engine-test conditions. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

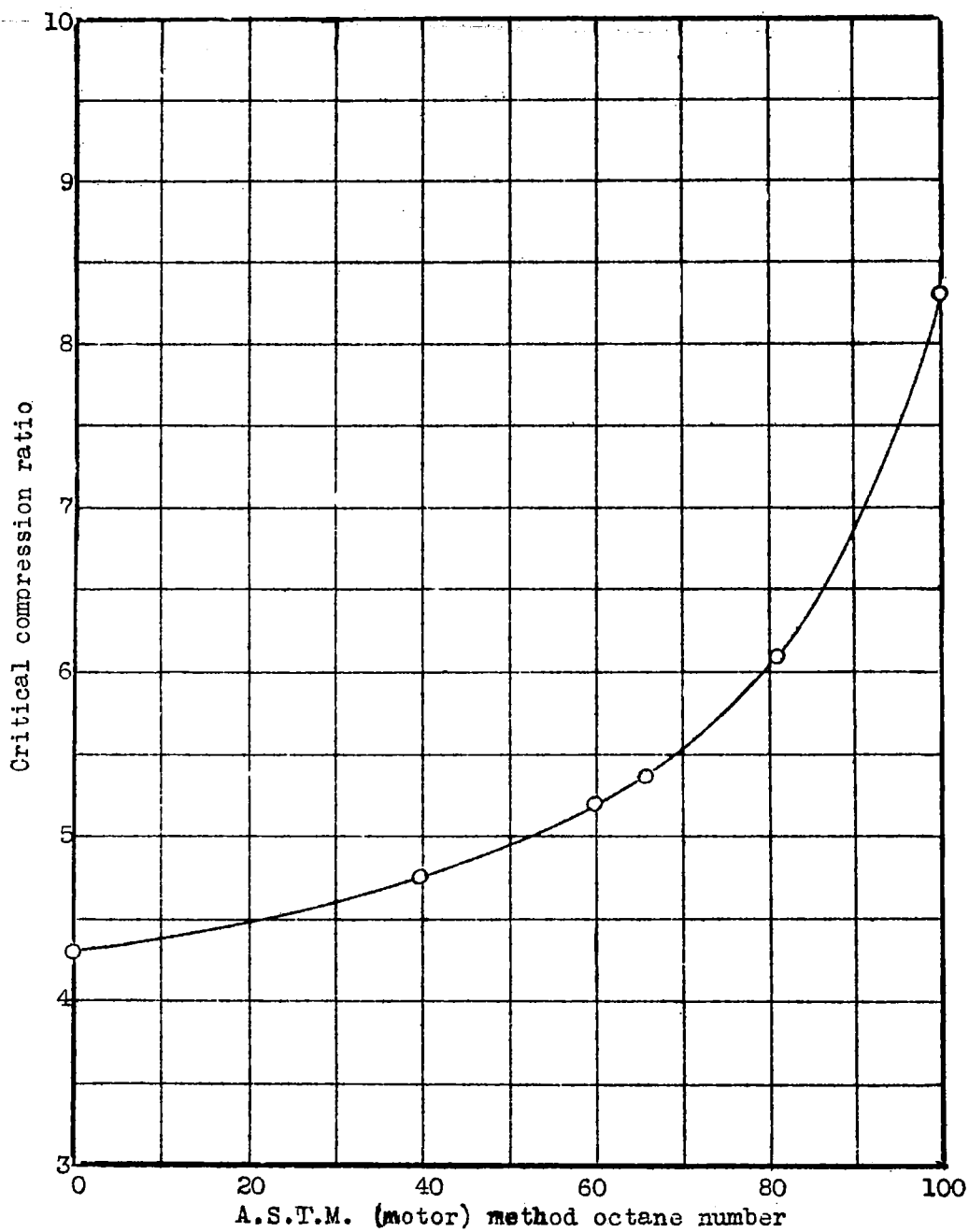


Figure 3.- Variation of critical compression ratio with A.S.T.M. (motor) method octane number.

Fig. 4

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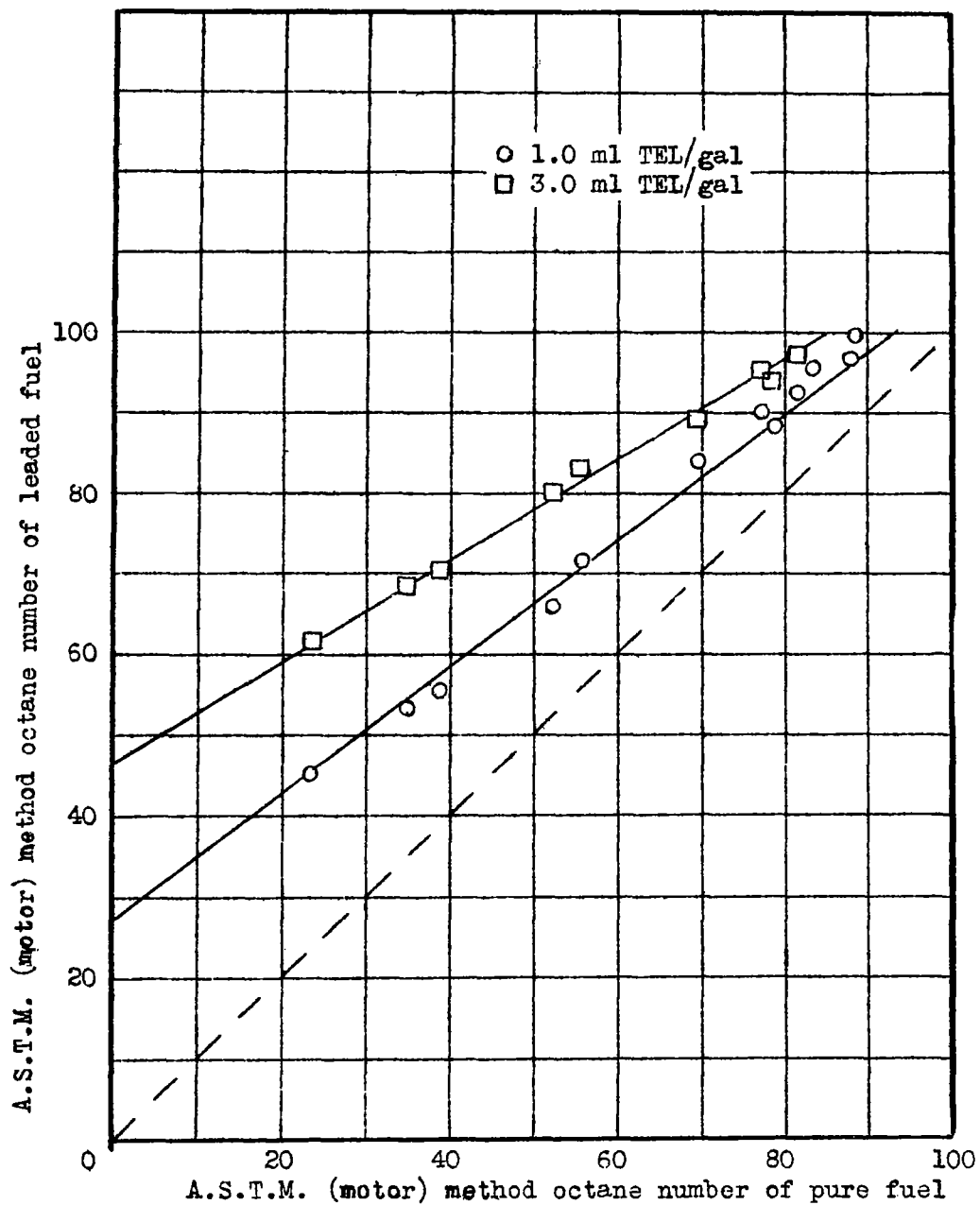


Figure 4.- Lead susceptibility of octanes.

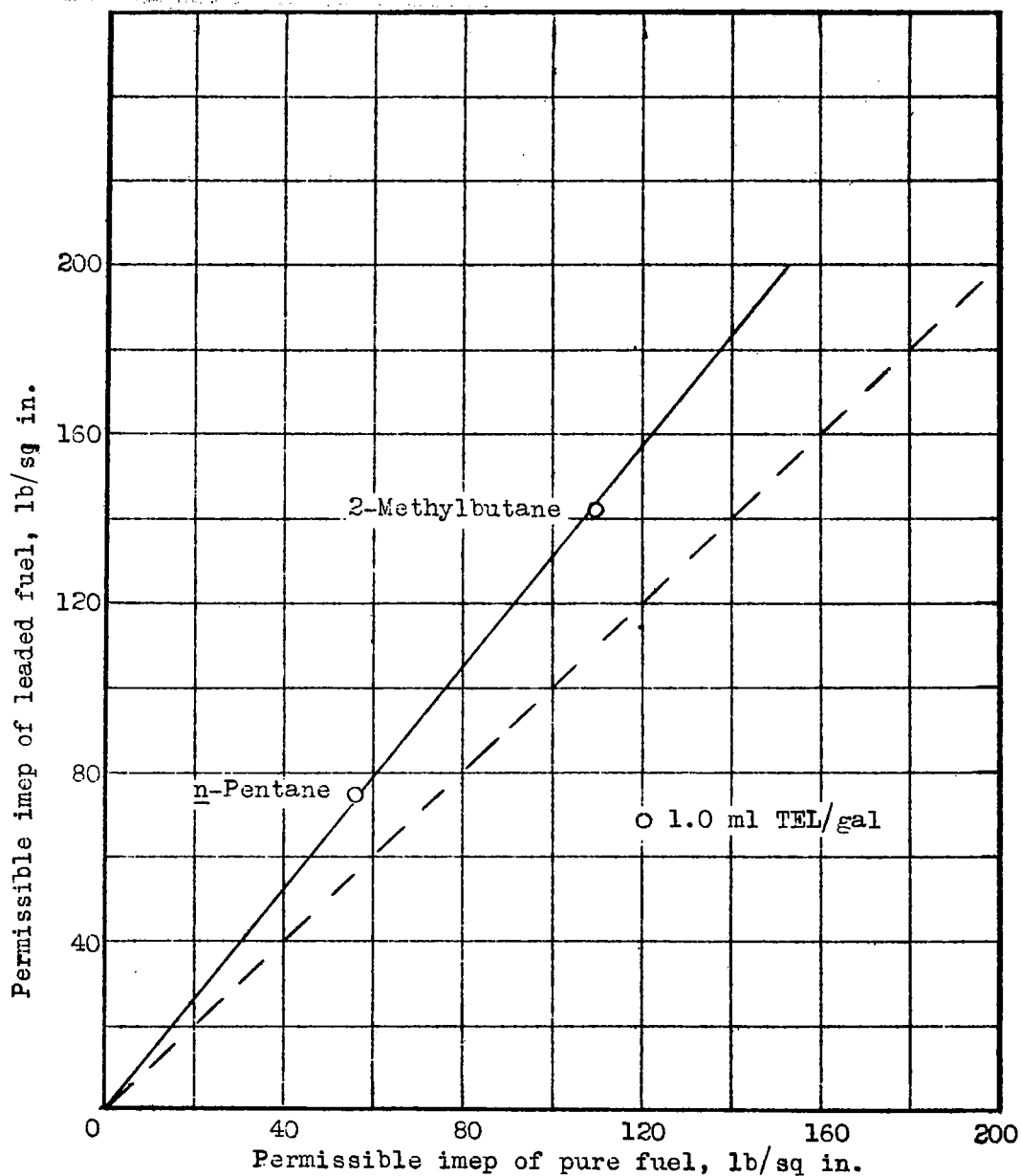


Figure 5.- Lead susceptibility of pentanes. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

Fig. 6

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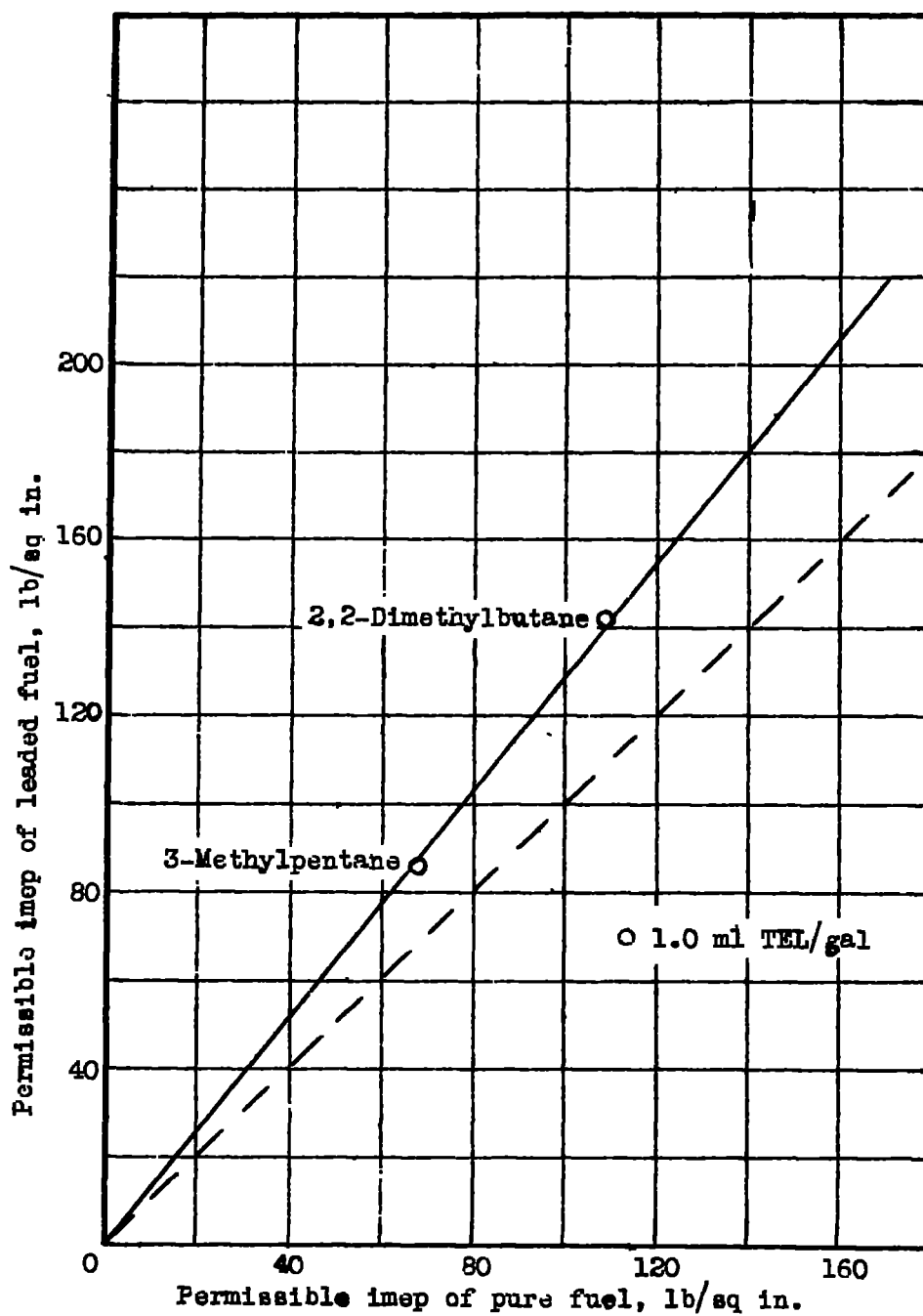


Figure 6.- Lead susceptibility of hexanes. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

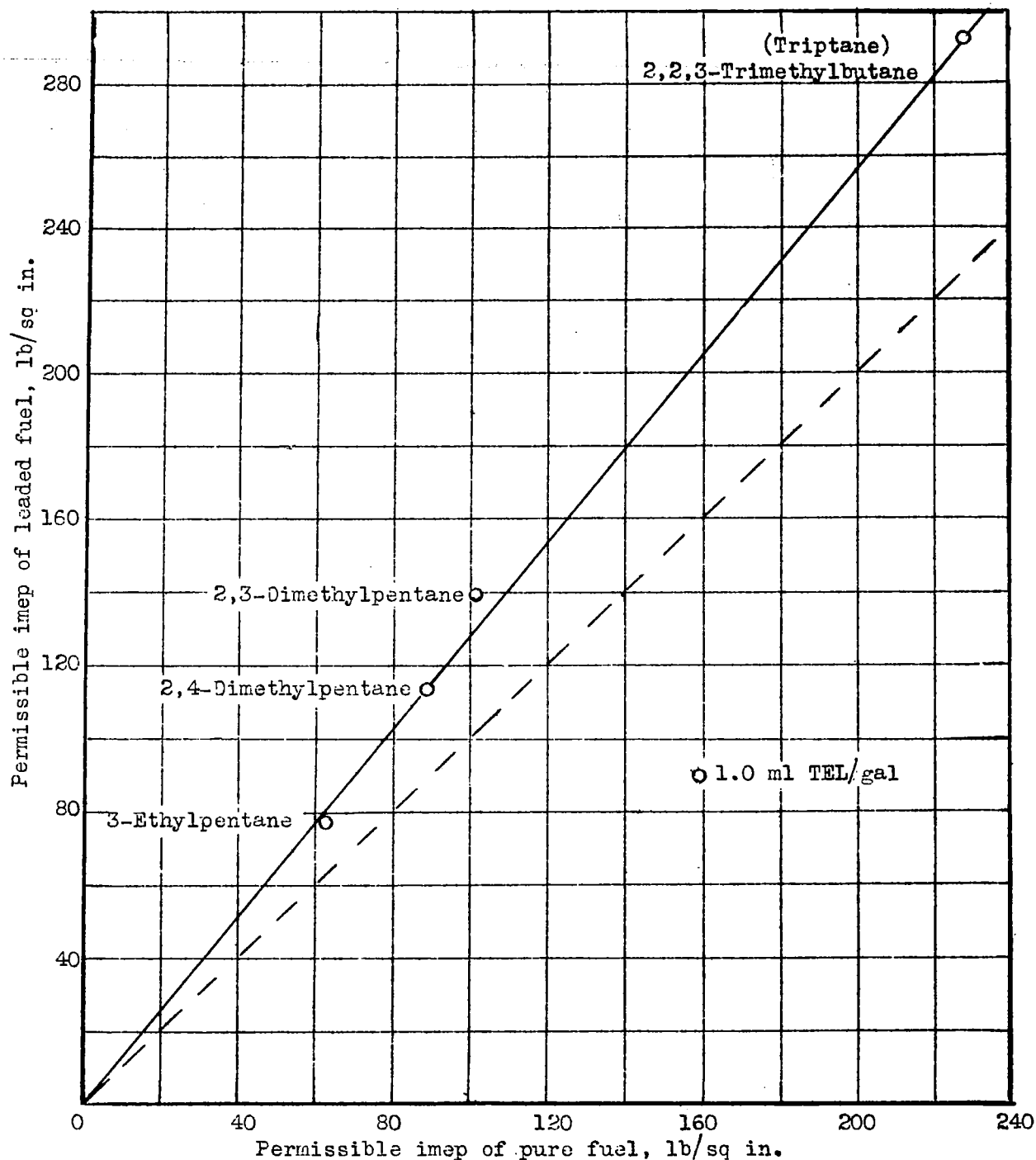


Figure 7.- Lead susceptibility of heptanes. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

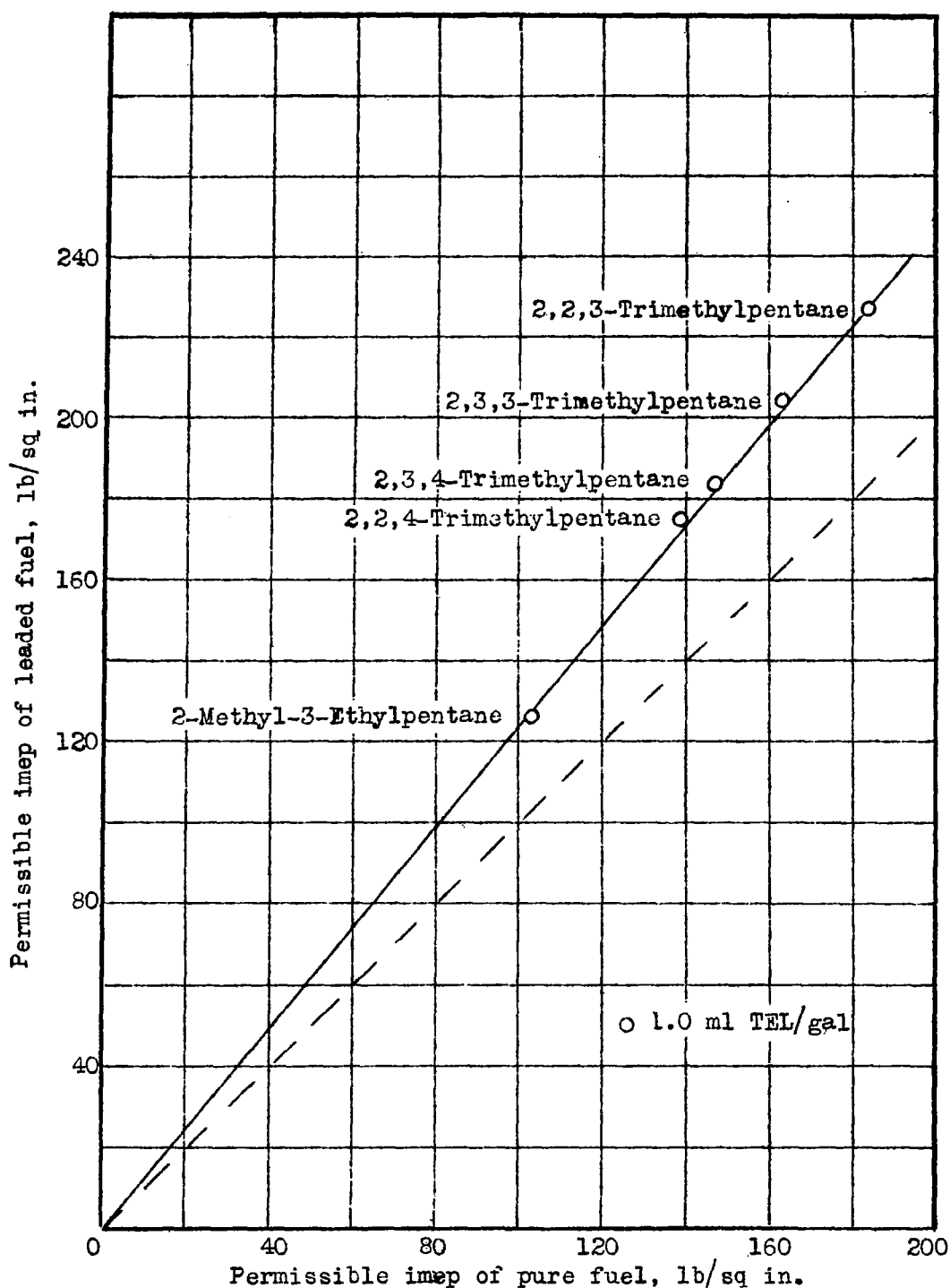


Figure 8.- Lead susceptibility of octanes. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.



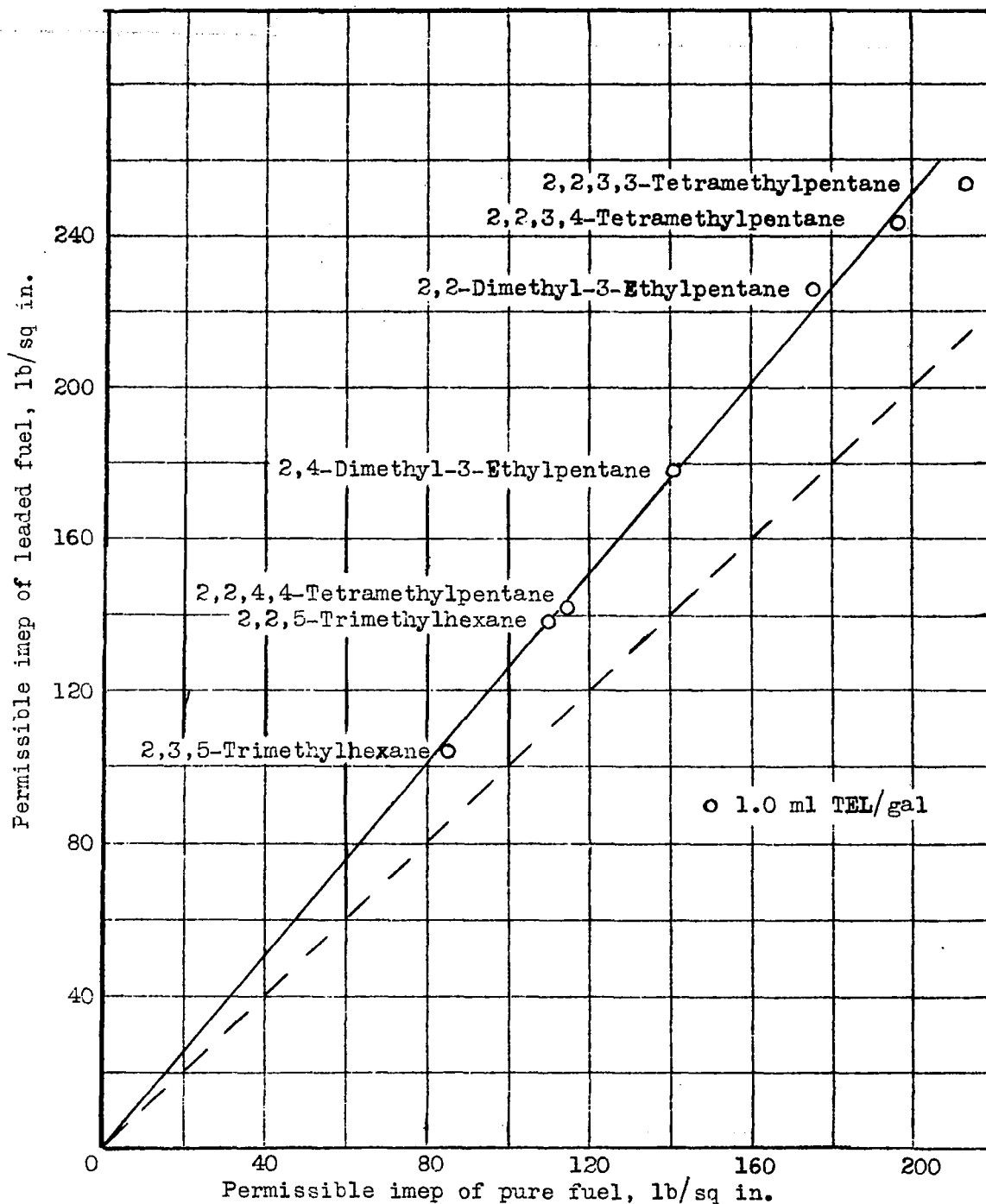


Figure 9.- Lead susceptibility of nonanes. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3^\circ \text{F}$ ; coolant inlet temperature,  $300 \pm 5^\circ \text{F}$ ; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

Fig. 10

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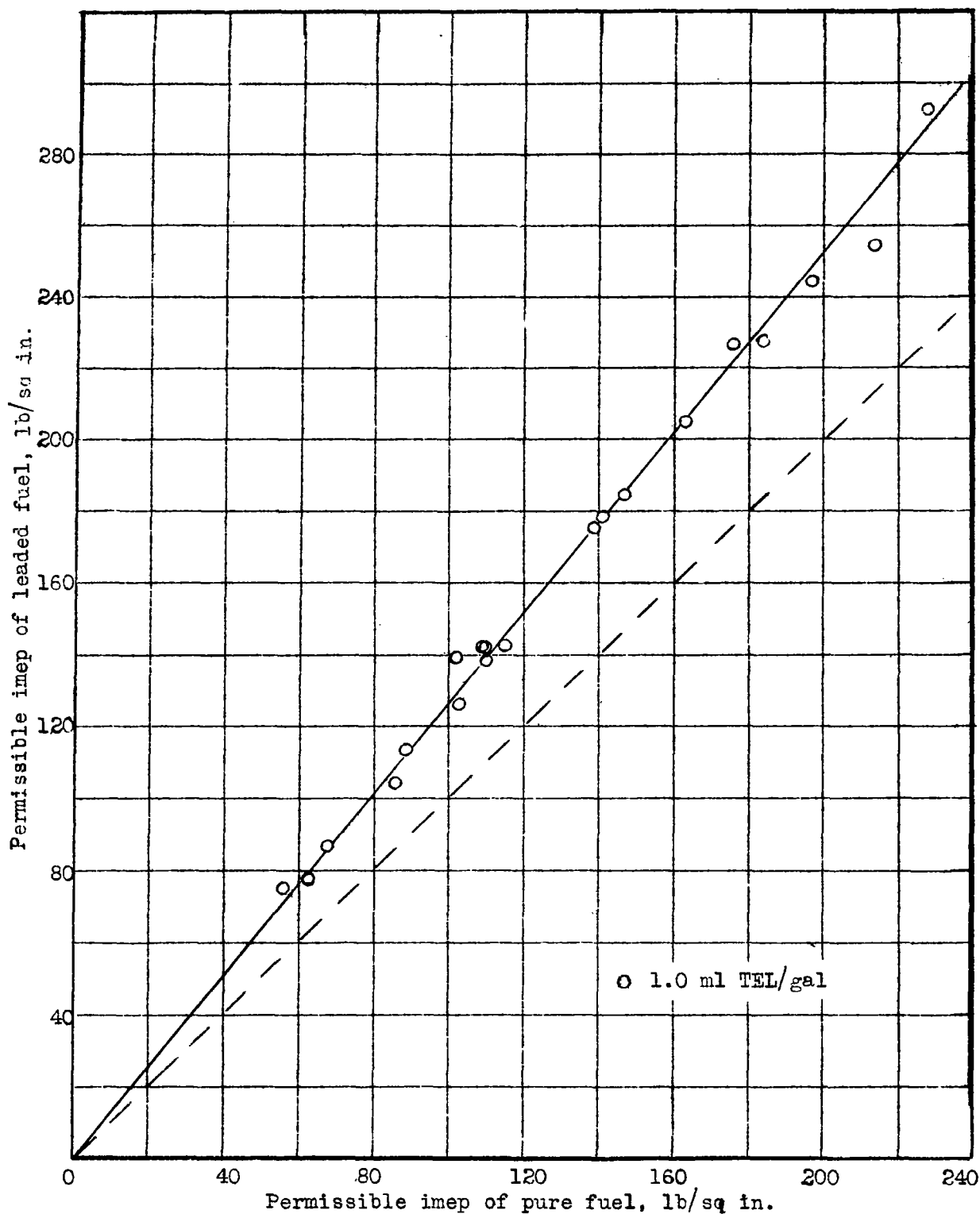


Figure 10.- Lead susceptibility of paraffinic hydrocarbons. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

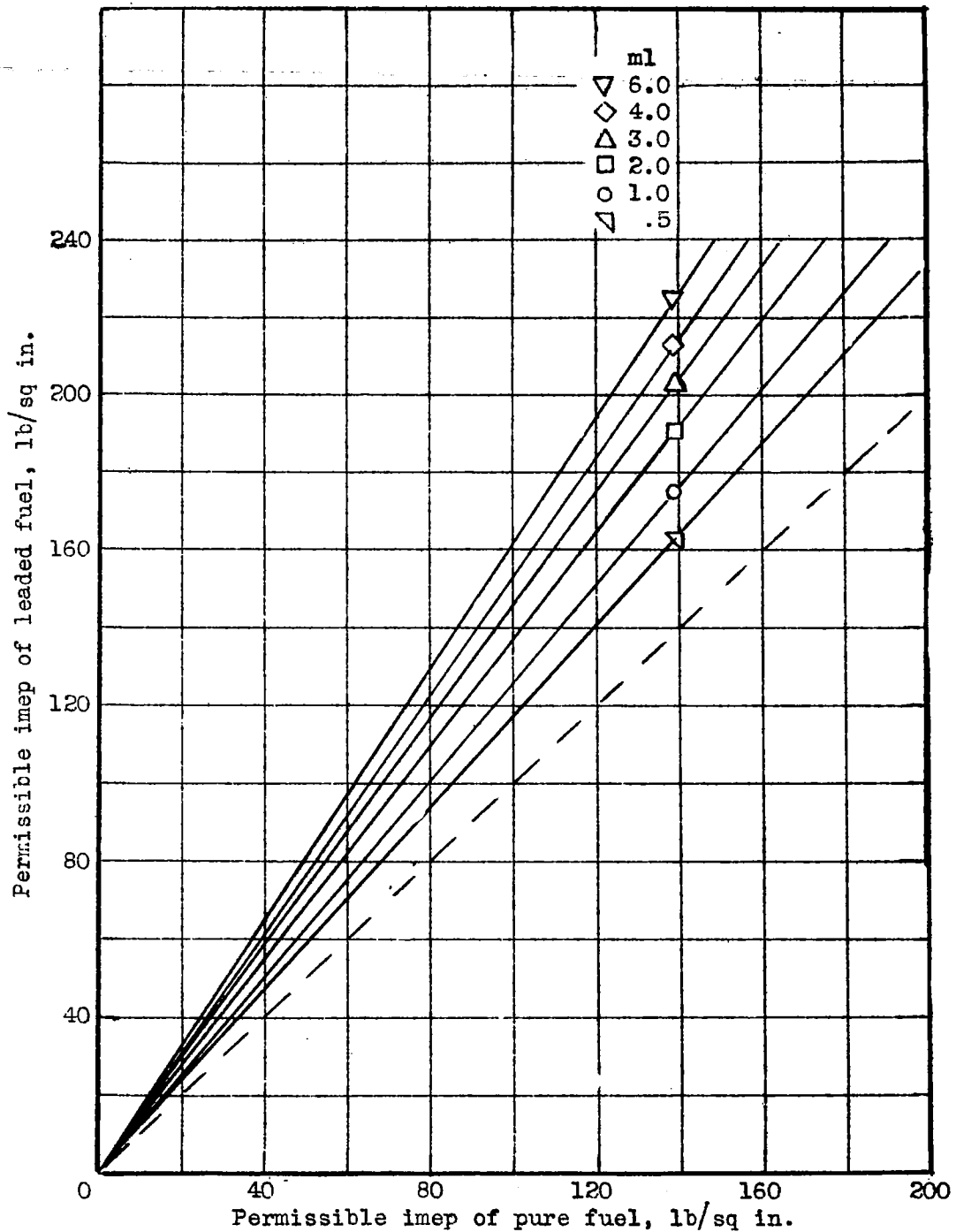


Figure 11.- Lead susceptibility of isooctane. The 17,6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

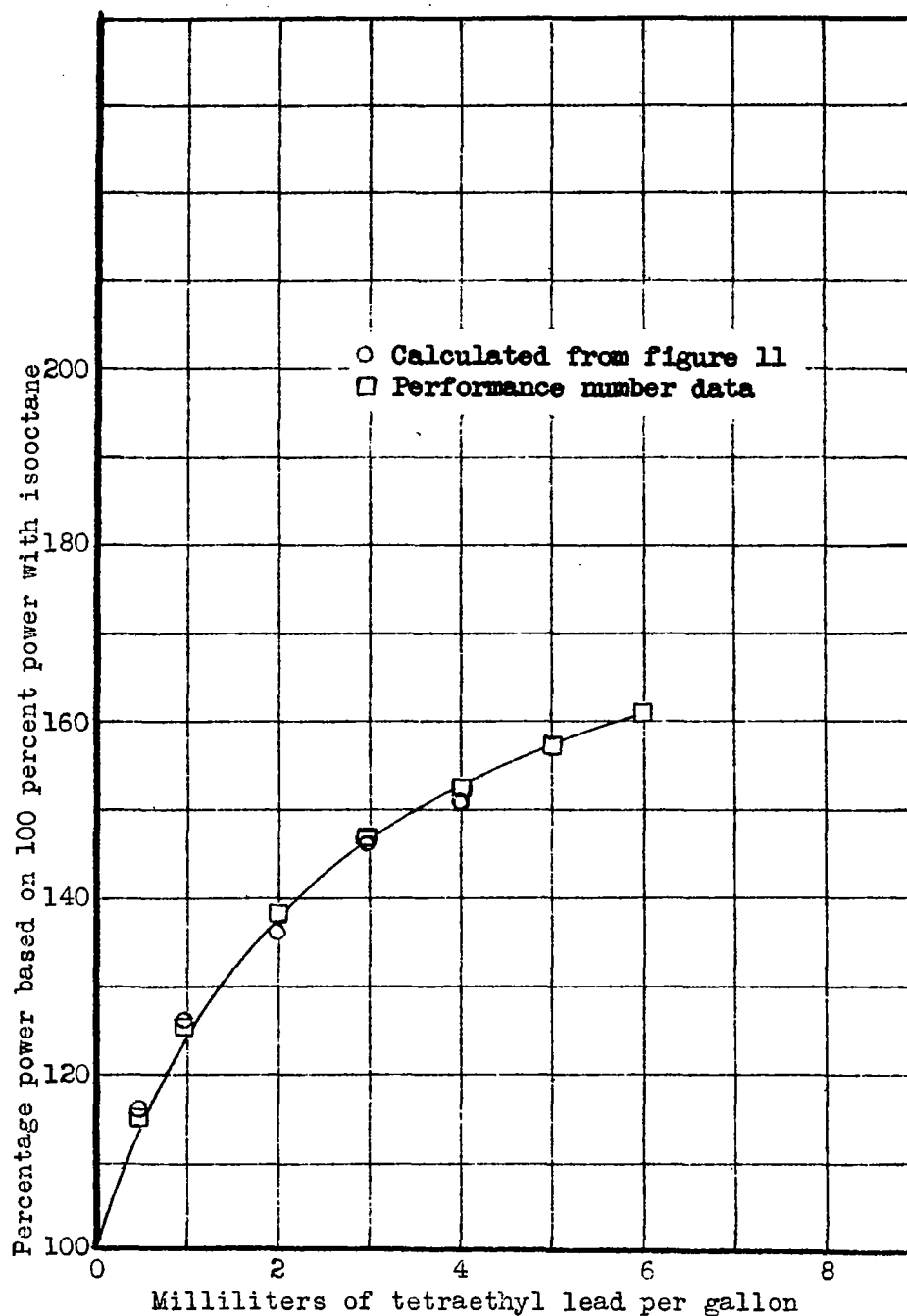


Figure 12.- Variation of power increase with tetraethyl-lead concentration for isooctane.

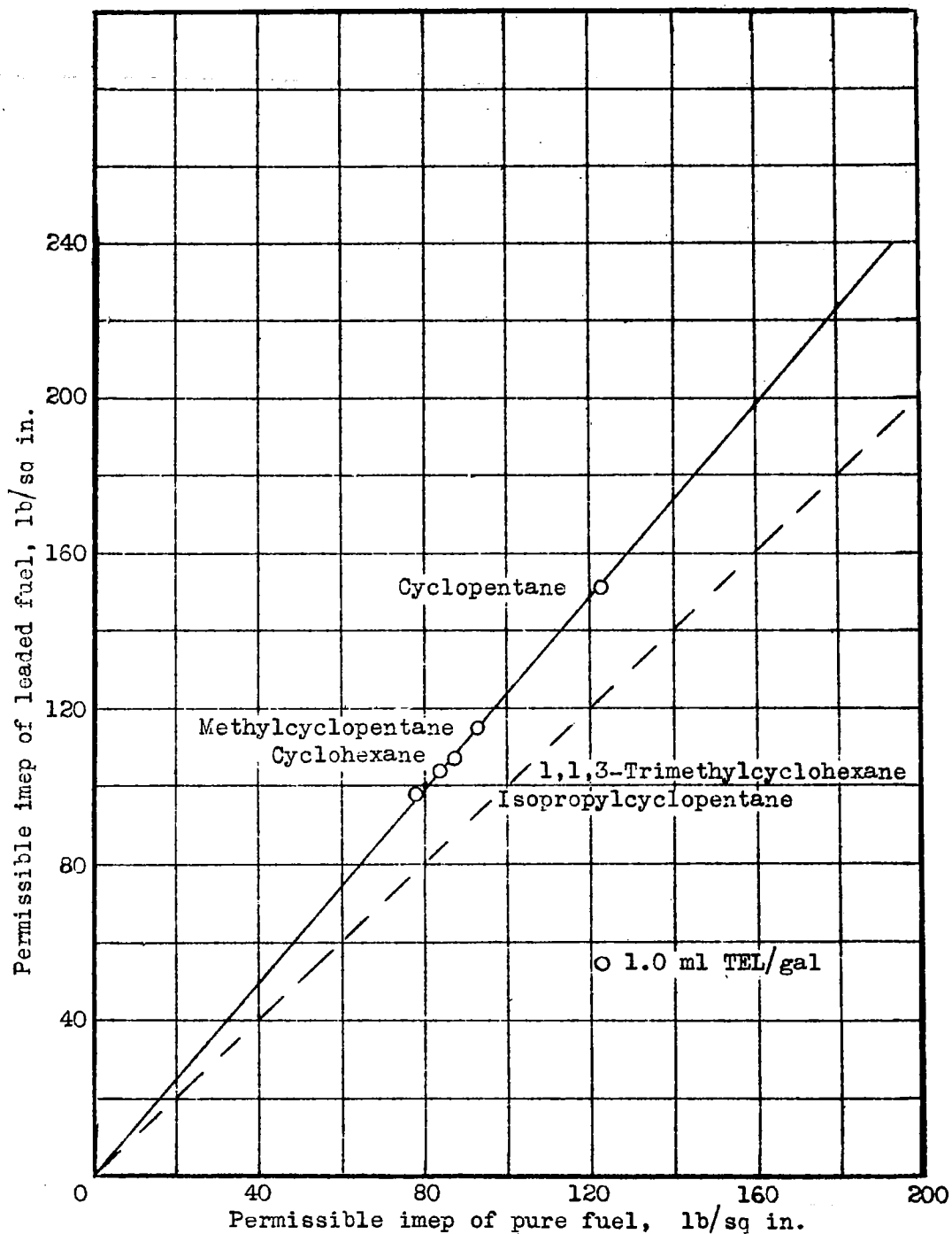


Figure 13.- Lead susceptibility of cycloparaffins. The 17.6 engine, engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

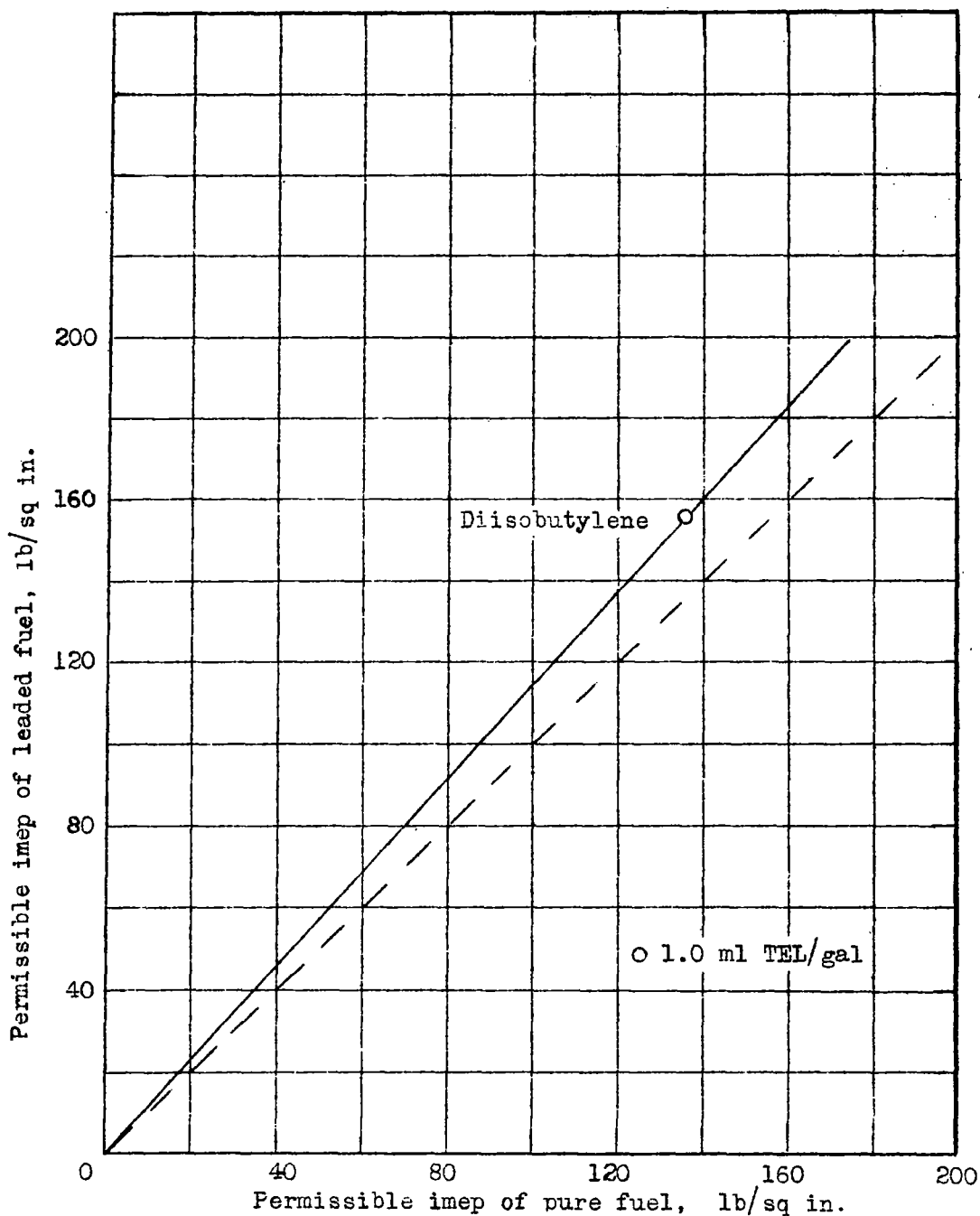


Figure 14.- Lead susceptibility of olefins. The 17.6 engine; engine speed, 900 rpm; intake-air temperature,  $225 \pm 3$  F; coolant inlet temperature,  $300 \pm 5$  F; compression ratio, 5.6; fuel-air ratio, approximately 0.070.

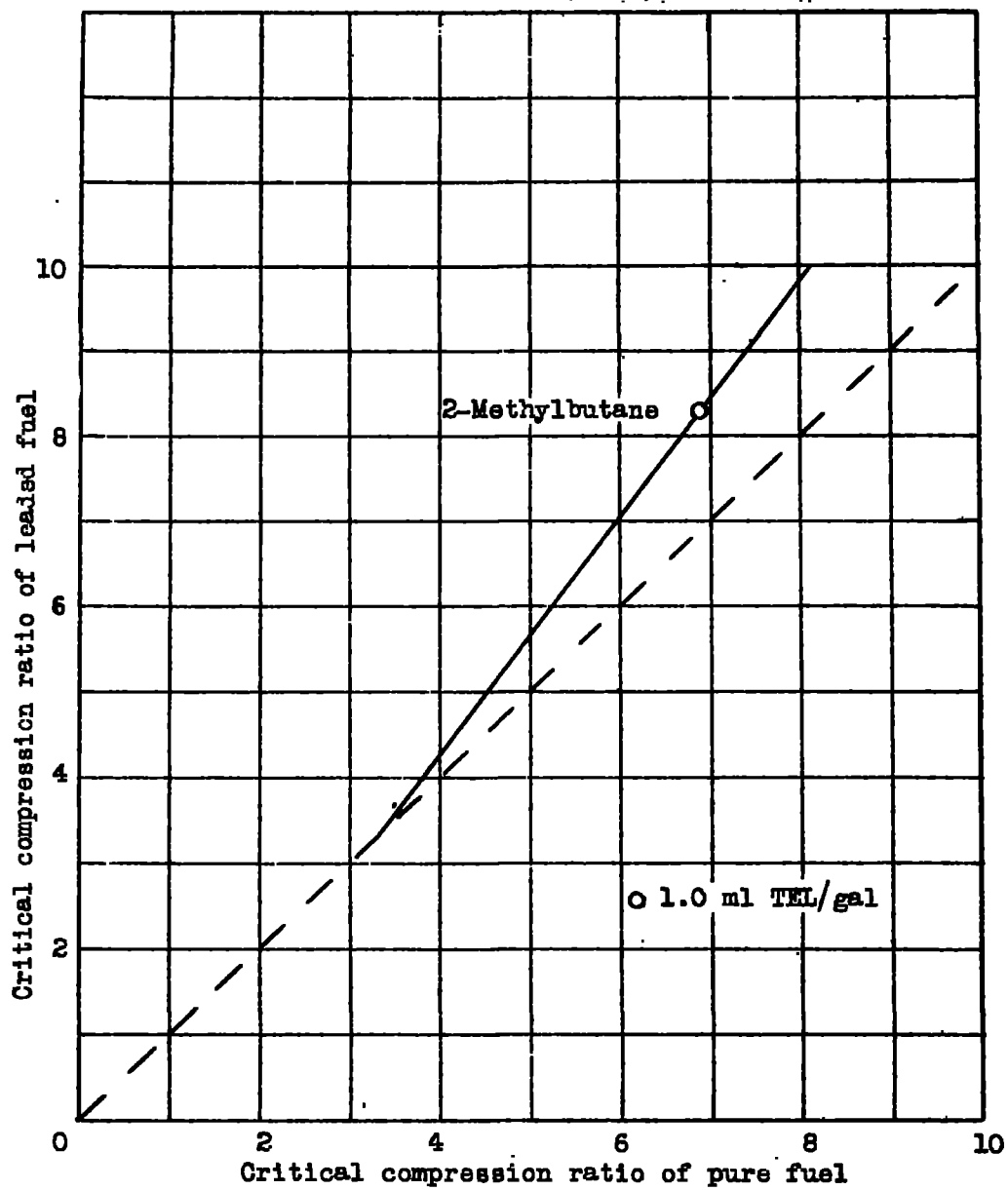


Figure 15.- Lead susceptibility of pentanes based on A.S.T.M. (motor) method ratings.

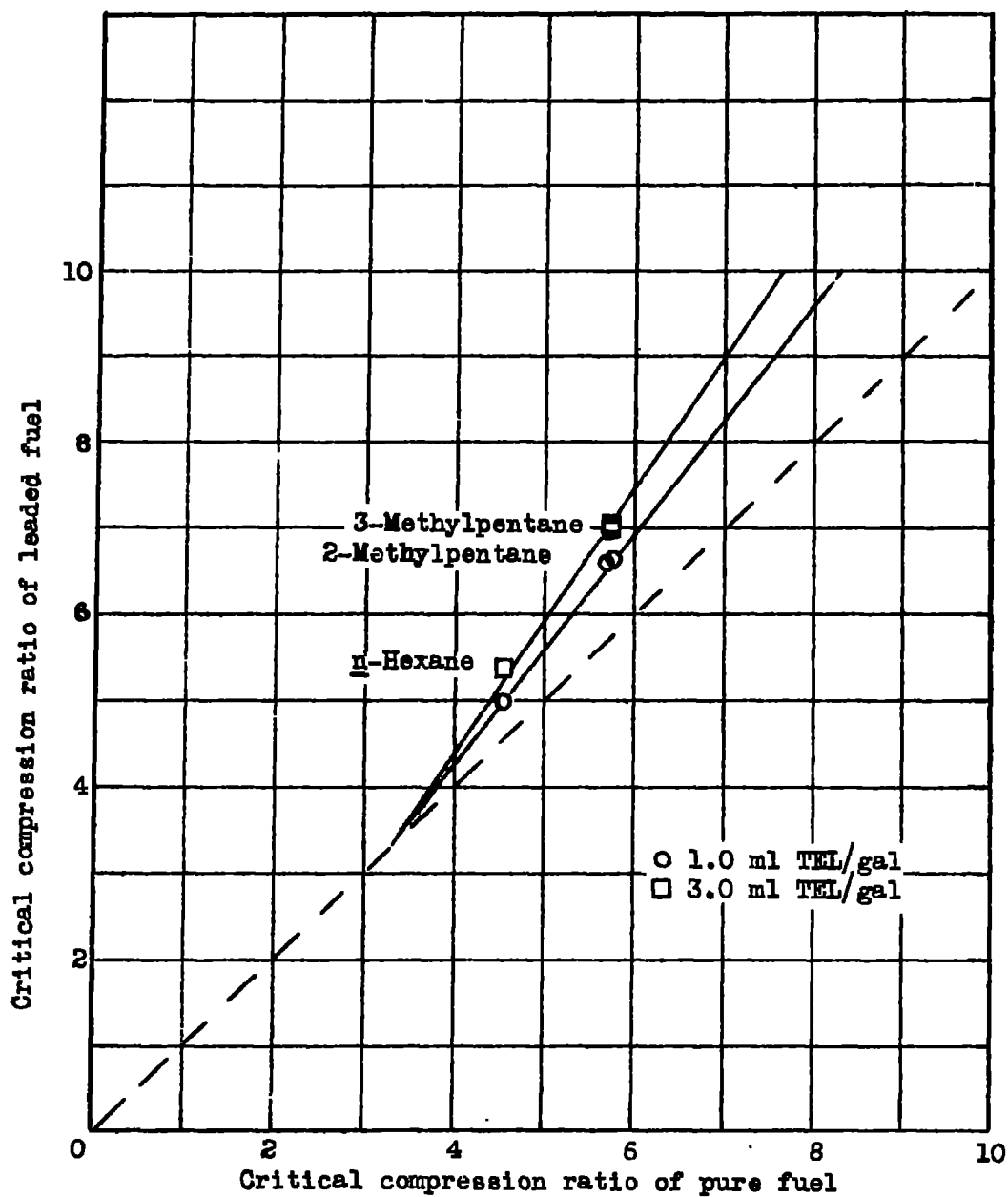


Figure 16.- Lead susceptibility of hexanes based on A.S.T.M. (motor) method ratings.



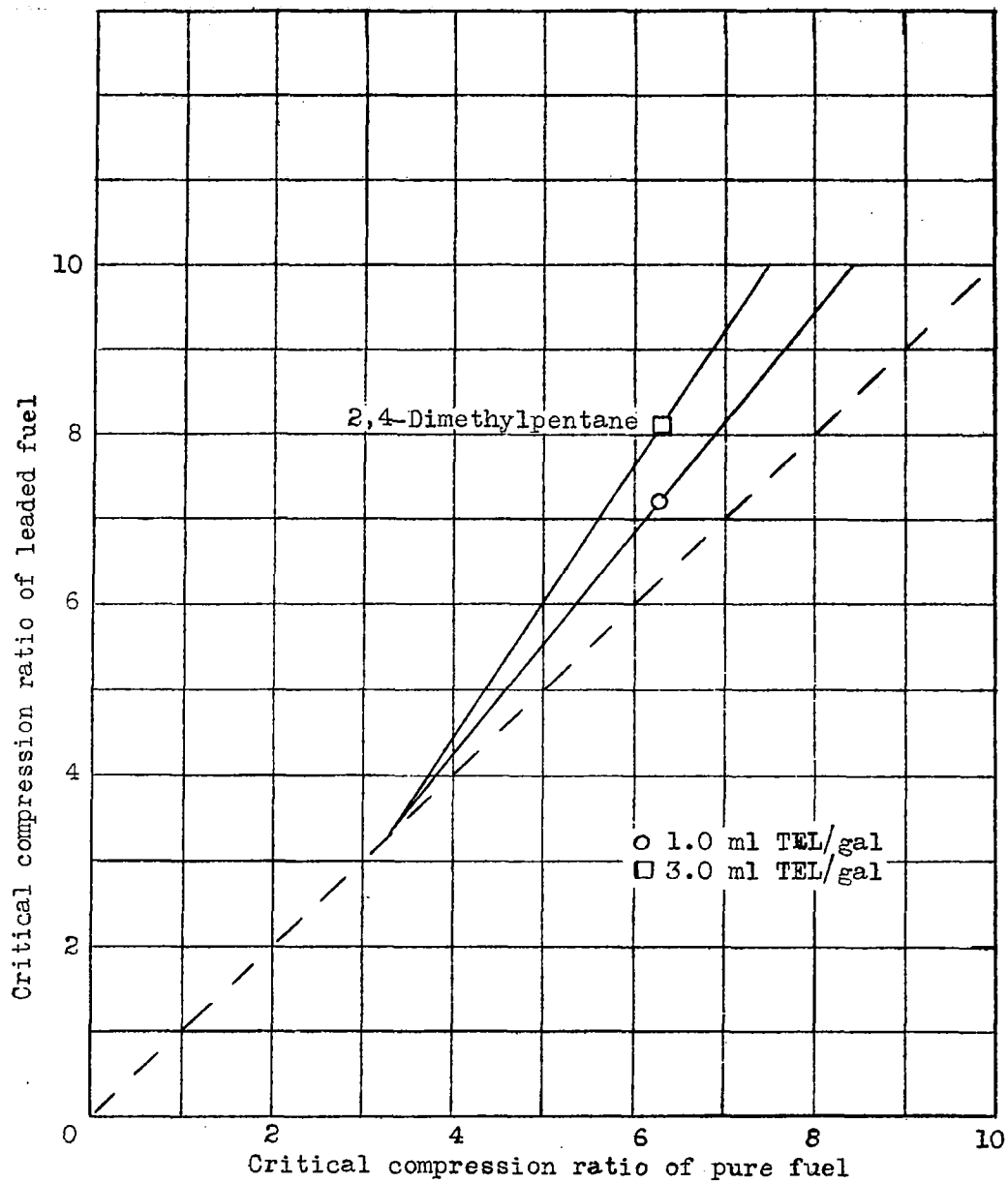


Figure 17.- Lead susceptibility of heptanes based on A.S.T.M. (motor) method ratings.

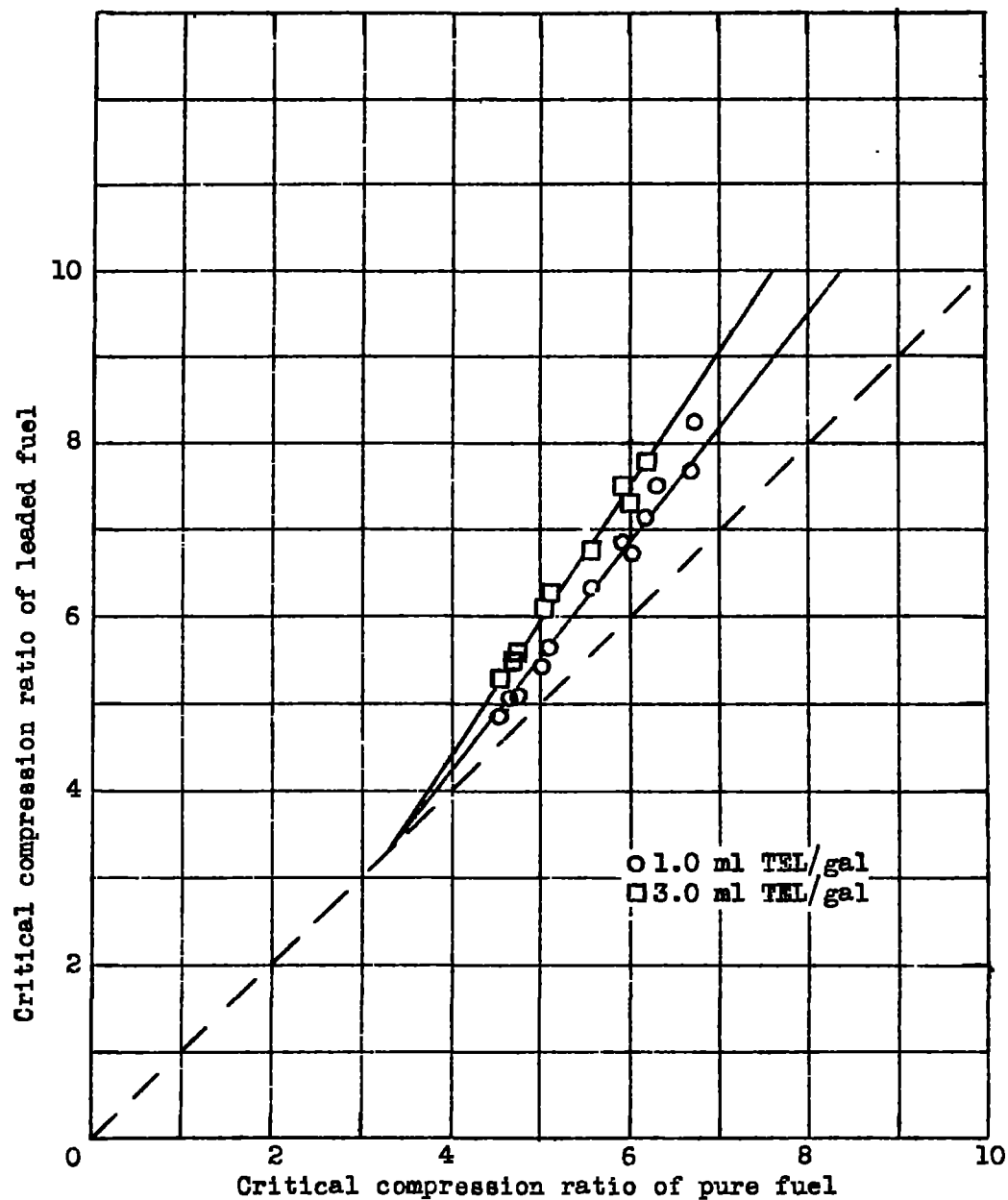


Figure 18.- Lead susceptibility of octanes based on A.S.T.M. (motor) method ratings.

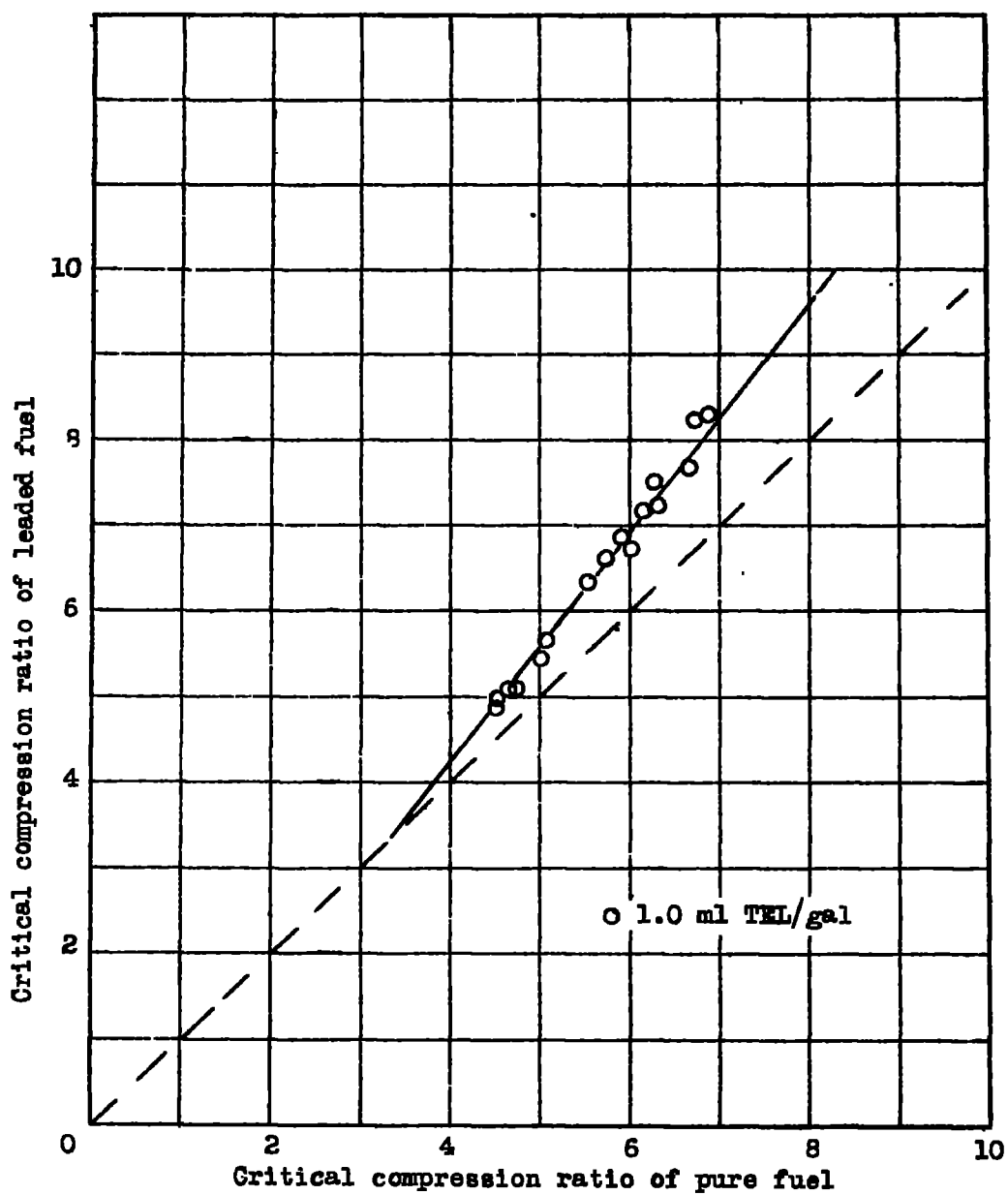


Figure 19.- Lead susceptibility of paraffins based on A.S.T.M. (motor) method ratings.

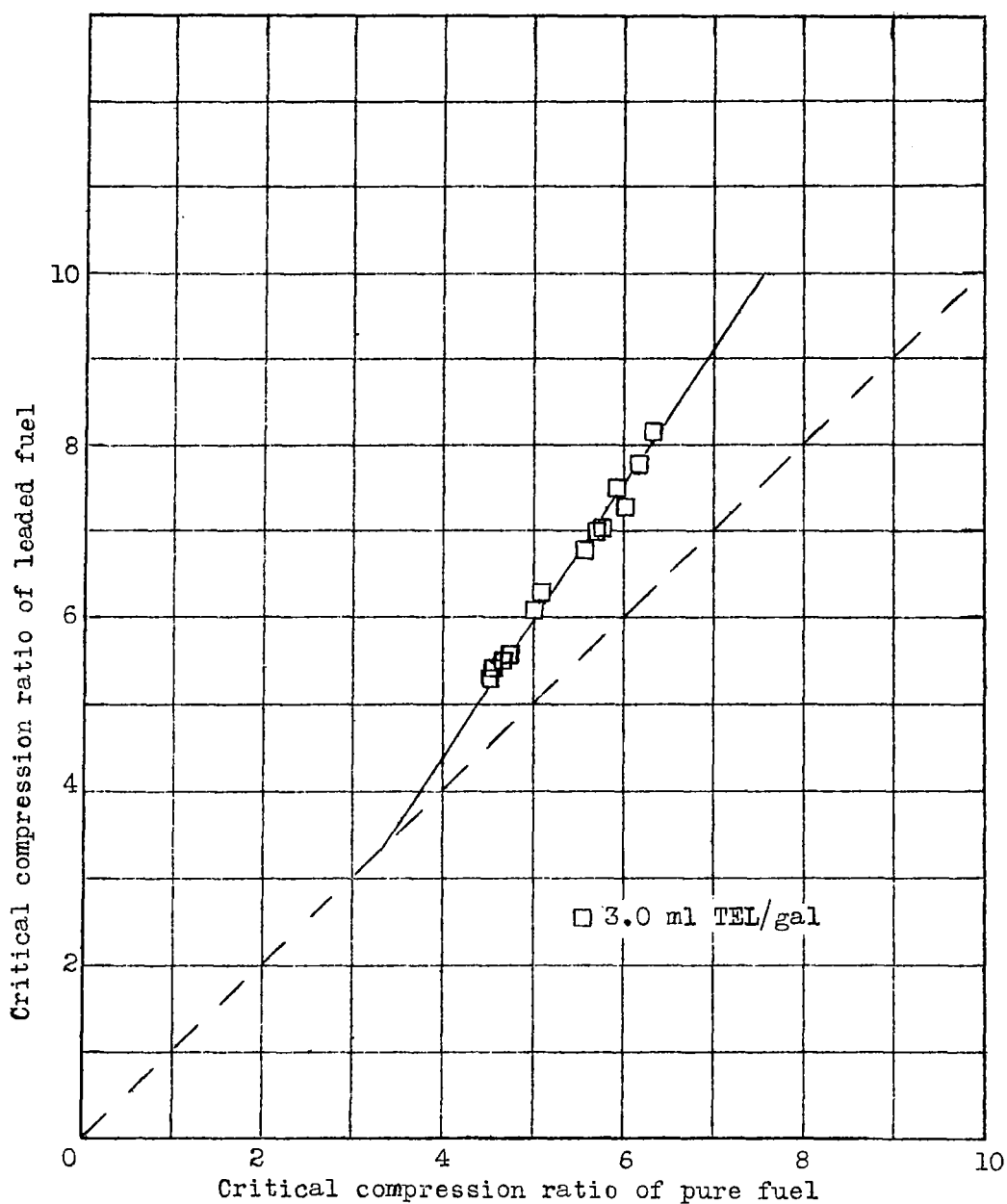


Figure 20.- Lead susceptibility of paraffins based on A.S.T.M. (motor) method ratings.

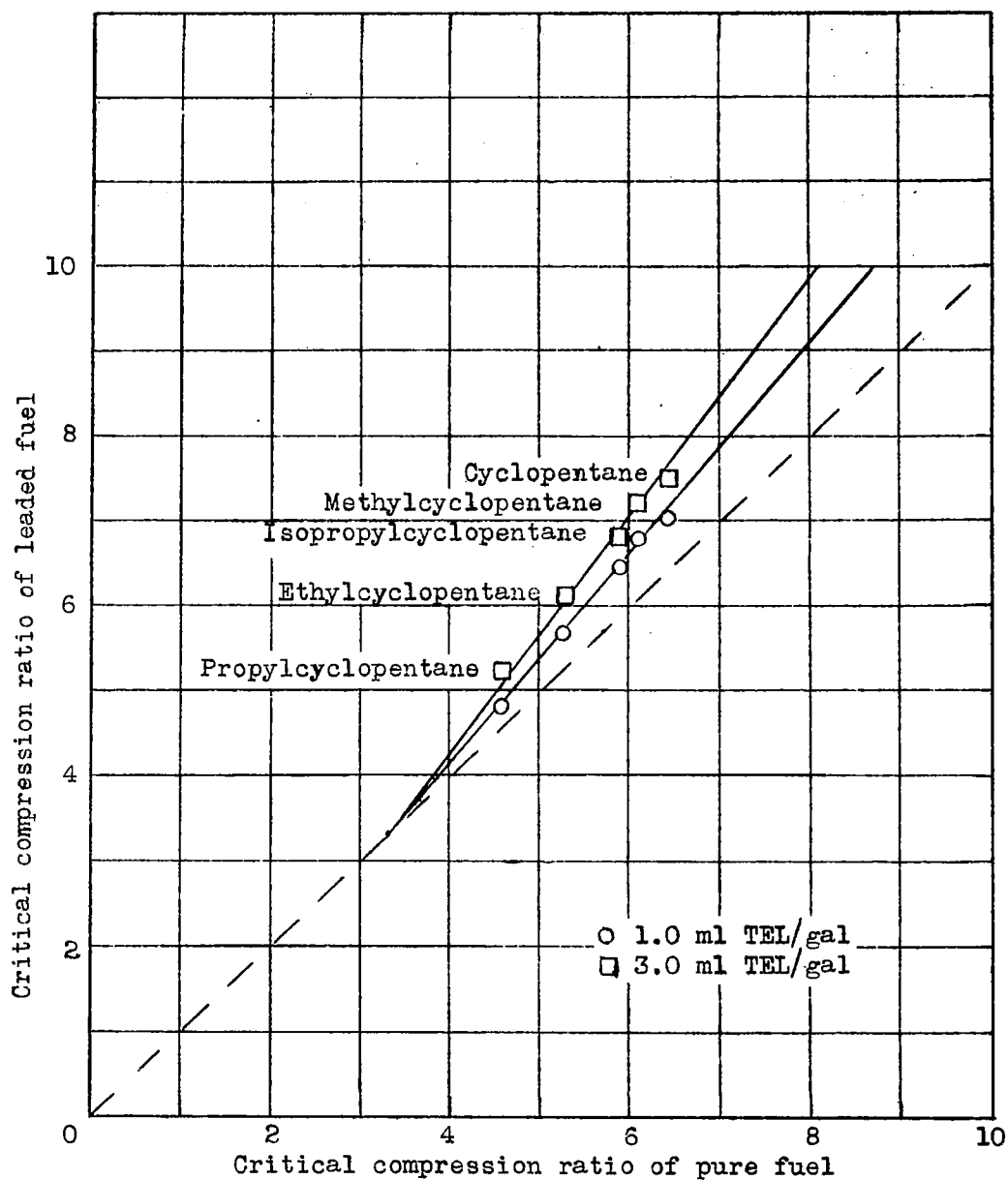


Figure 21.- Lead susceptibility of cyclopentane derivatives based on A.S.T.M. (motor) method ratings.

Fig. 22

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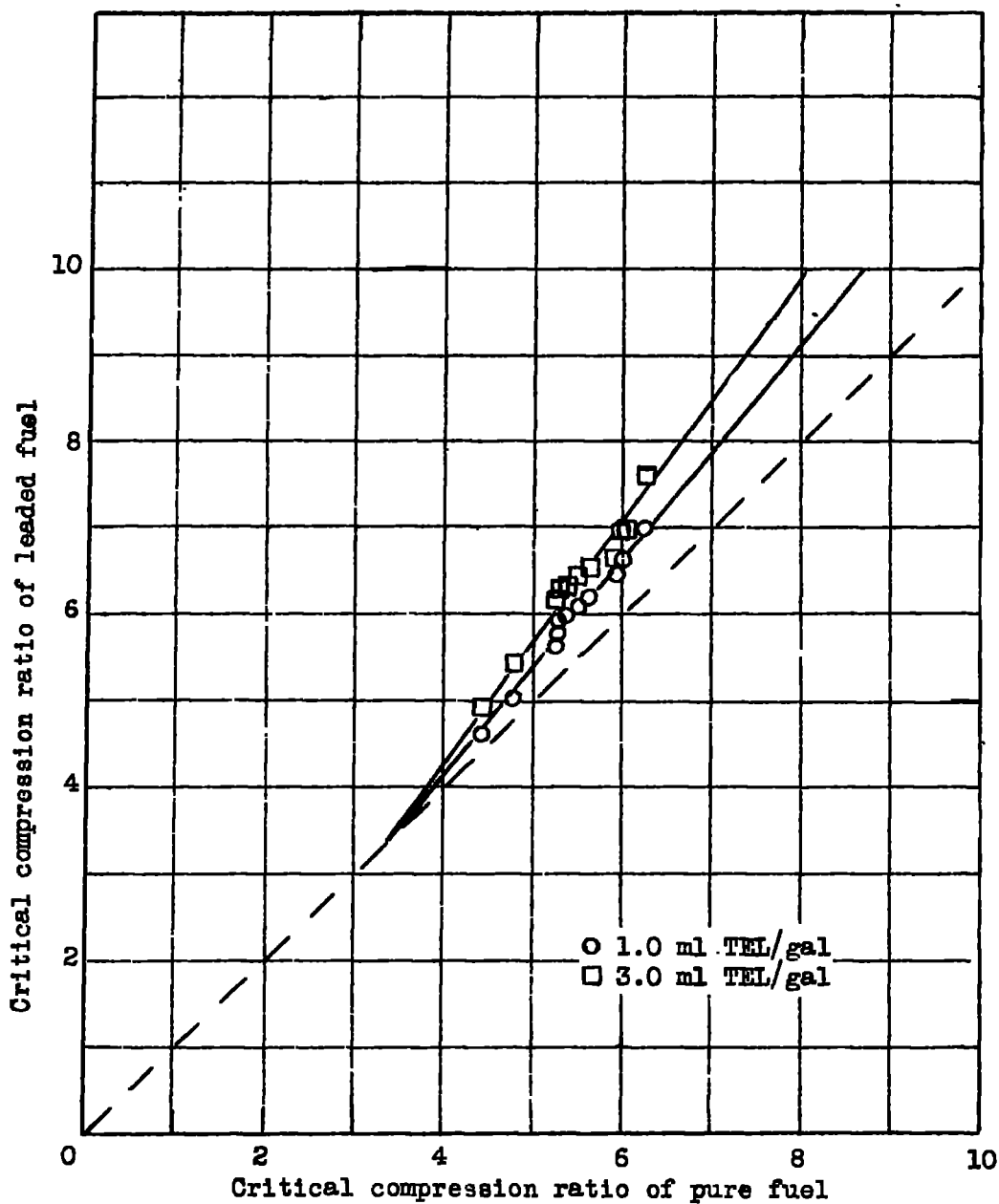


Figure 22.- Lead susceptibility of cyclohexane derivatives based on A.S.T.M. (motor) method ratings.

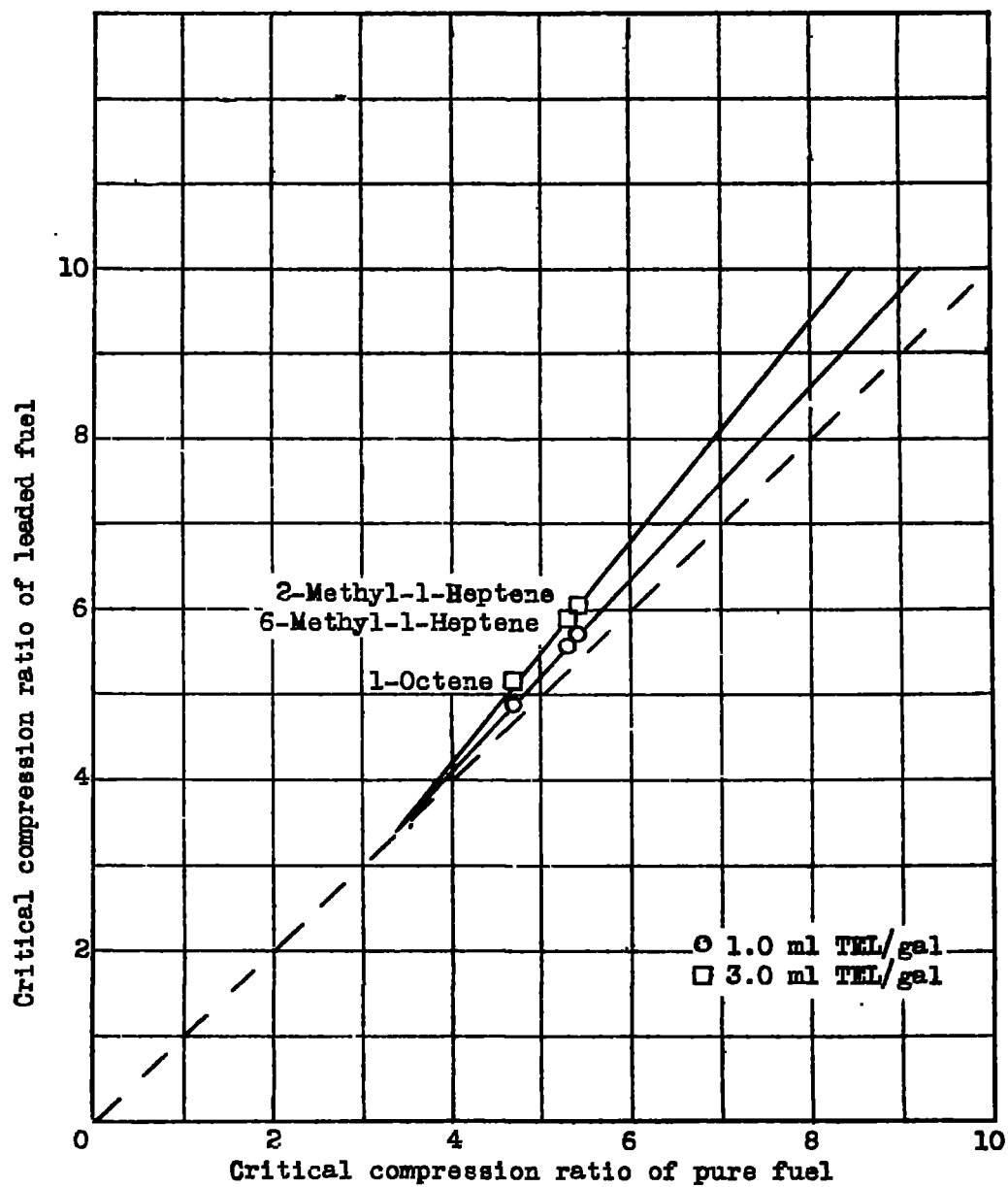


Figure 23.- Lead susceptibility of octenes based on A.S.T.M. (motor) method ratings from reference 1.

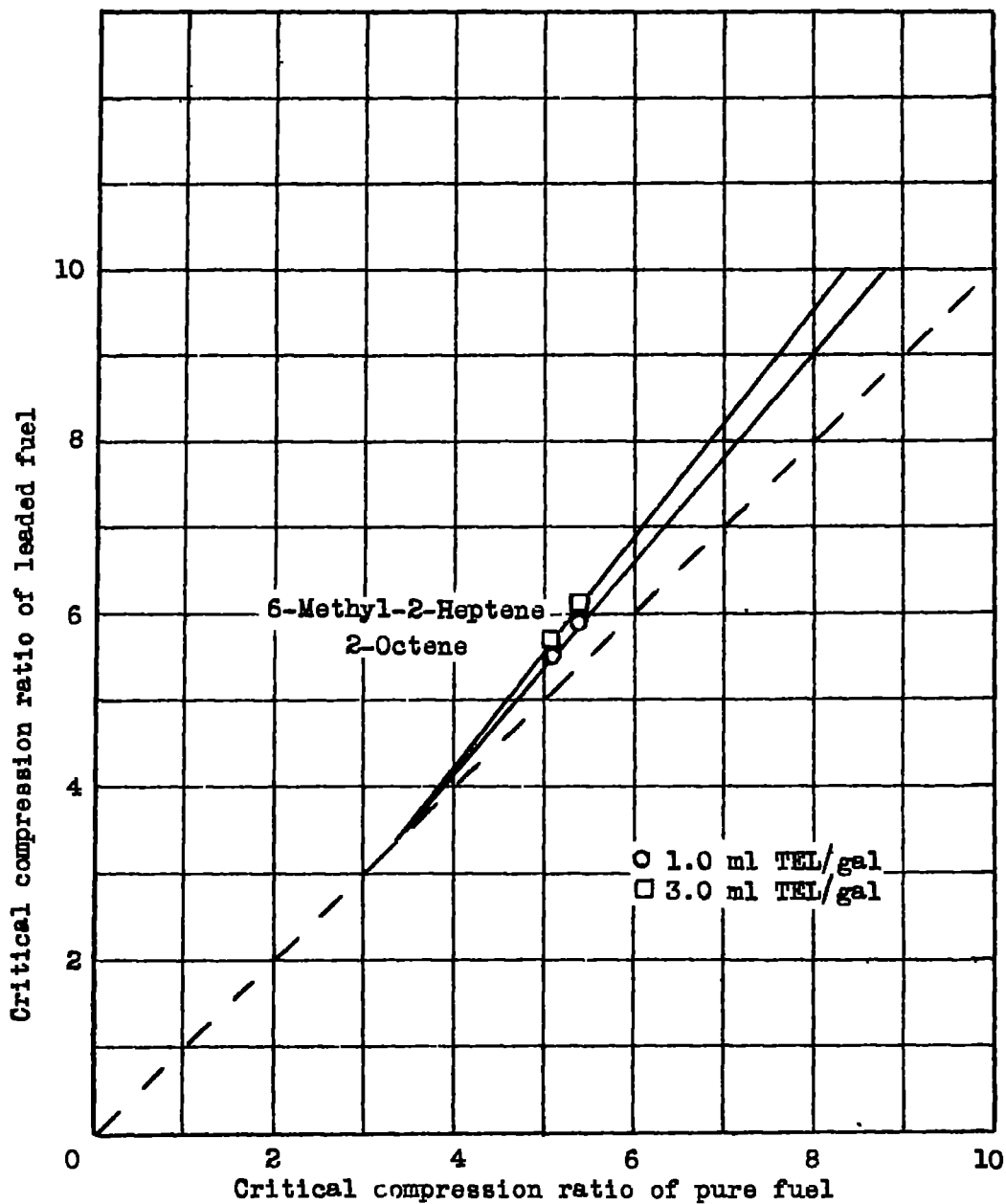


Figure 24.- Lead susceptibility of octenes based on A.S.T.M. (motor) method ratings.



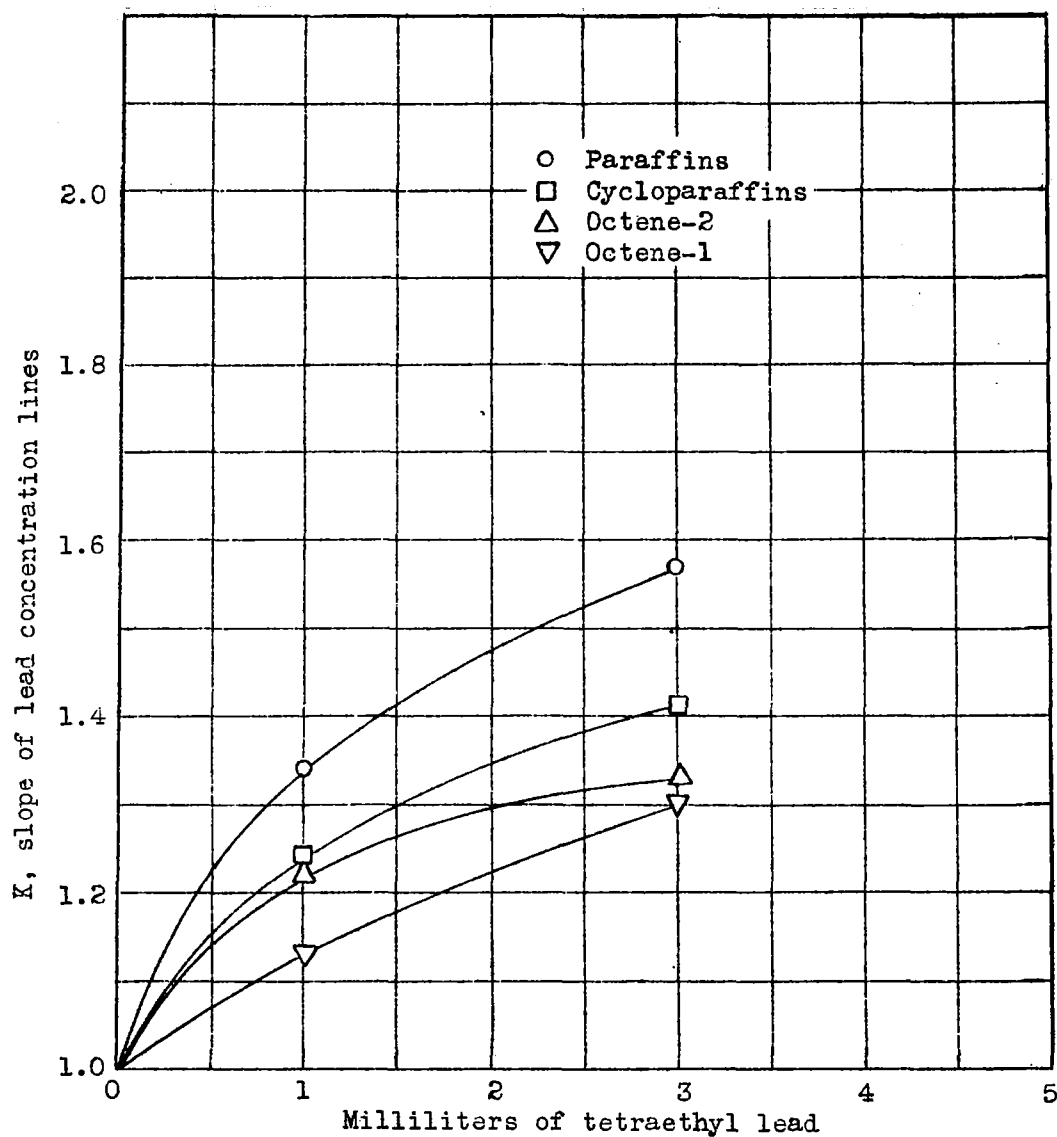


Figure 25.- Variation of K, slope of lead concentration line, with tetraethyl-lead concentration.

Fig. 26

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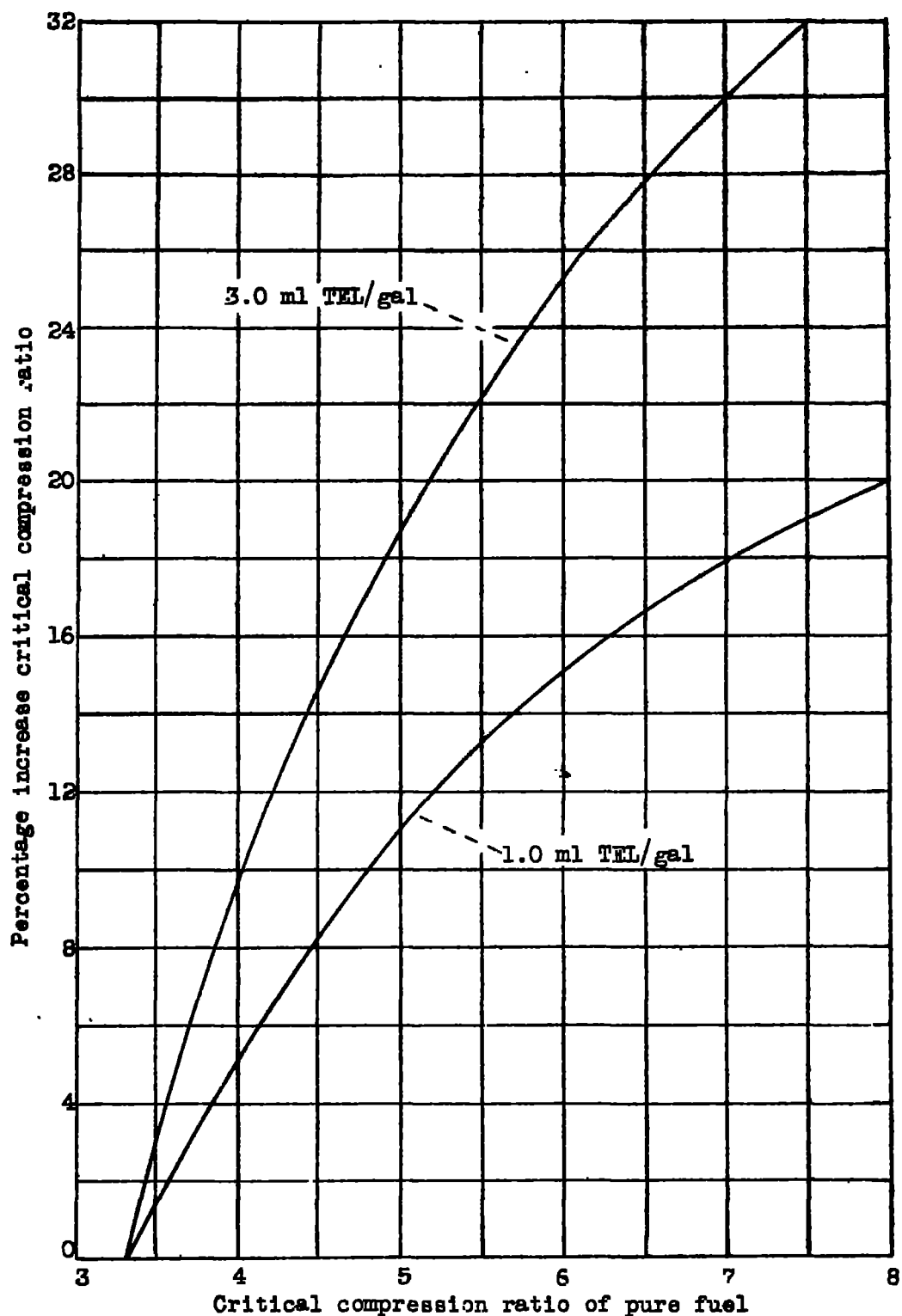


Figure 26.-- Variation of percentage increase in critical compression ratio with critical compression ratio of pure paraffins.

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